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## CHARACTERIZATION OF HIGHLY DISPERSED PHASES IN POLYMER BLENDS

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Blending of chemically different polymers is an attractive way to optimize the mechanical or permeability properties of polymeric materials. A full use of its possibilities depends, however, on several key points: control of dispersion and its stabilization for further processing by using such means as thermodynamic control by surface-active agents, as block copolymers, or interfacial chemical reaction between the two species; a better understanding of the dependence of the properties on the size and shape of the dispersion, including the possibility of bicontinuous structures.

Central to these points is characterization of the blend morphology. Direct imaging by optical or electron microscopy is limited to dispersions with sizes of the same order as the smallest achievable thickness of a sample slice. For smaller dimensions, scanning electron microscopy (SEM) of surfaces of cryofracture is often difficult to analyze. X-ray (or neutron) diffraction suffers problems of contrast and theoretical interpretation.

Practical industrial blending is generally achieved by mechanical mixing prior to or during processing, generally in the presence of a third component. The system seldom reaches a state of thermodynamical equilibrium. Laboratory preparation of blends is often made through evaporation or lyophilization of solutions of the two polymers in a common solvent. Even in cases where the bulk polymers are compatible, phase separation can arise during the concentration or cooling step. Blends in a high state of dispersion can be obtained in cases where phase separation of a compatible molten phase can be achieved by spinoidal decomposi-

tion when heated above the lower critical solution temperature (LCST) or below the upper critical solution temperature (UCST) and then rapidly quenched below  $T_g$ . In the case of LCST, regression of the spinoidal separation can take place through annealing at temperatures just above  $T_g$ .

DSC experiments have proved very useful for demonstrating phase separation. The presence of two distinct  $T_g$ 's can be resolved even when they are very close by using the procedure introduced by Ten Brinke [2] who submits the glassy sample to a physical aging which transforms a shift in the baseline, typical of the change in  $C_p$  at  $T_g$ , into an enthalpic peak, the origin of which has been clarified by Kovacs [3]. But this gives only information on the existence of large enough "phases" to display a macroscopic  $T_g$  close to that of the pure constituents. The minimum size required is not clear.

In what follows we present two approaches to the characterization of the size of highly dispersed systems in the molten or glassy state, the methodology of which is currently being developed in our laboratory. The molten state characterization relies on rheological experiments. The solid-state characterization relies on NMR measurements. Only the basic principles of the methods and some results of their application will be described, with references to the original papers, published or to be published.

## RHEOLOGY OF INCOMPATIBLE BLENDS IN THE MOLTEN STATE

The transformation of an incompatible fine dispersion of two Newtonian liquids into a viscoelastic material is well illustrated by the mixing of oil and vinegar into a mayonnaise, egg yolk playing the role of the surfactant. The resulting viscoelastic behavior, i.e., the appearance of a real part  $G'$  in the shear modulus, is related to the deformation of the droplets which store some elastic energy. Similarly, blends of two incompatible viscoelastic phases can present a characteristic increase of  $G'$  above that of the constituents (Fig. 1). In the low frequency range, corresponding in the time domain to times longer than the "terminal" time of the individual constituents, i.e., where they essentially flow like Newtonian liquids, this increase of  $G'$  can be analyzed by using theories developed for Newtonian liquids as a function of the viscosity of the constituents and the ratio  $\alpha/R$  of the interfacial tension  $\alpha$  and radius  $R$  of spherical droplets [4]. The general calculation of the frequency

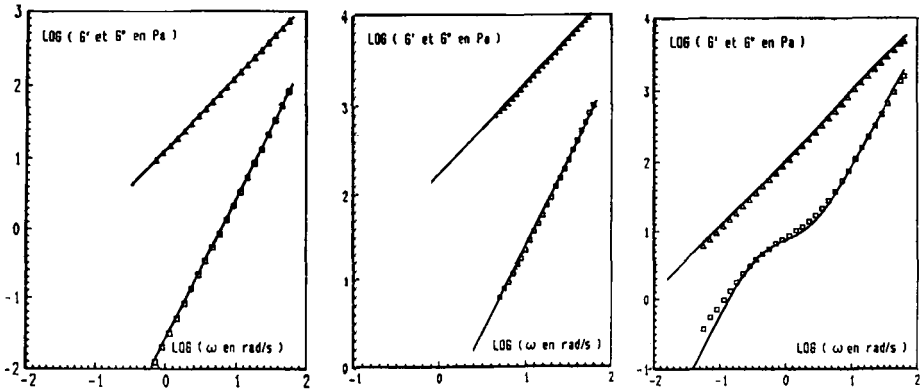


FIG. 1. Shear modulus of the PEO inclusions, PDMS matrix, and a 20% blend at 70°C. The lines correspond to a Maxwell model for the pure polymers and to the Palierne model for the blend with  $\alpha = +0.4$  mN/m and a distribution of sizes with  $R_n = 15 \mu\text{m}$  and  $R_w = 20 \mu\text{m}$ .

dependence of the complex shear modulus in the full frequency range and for an arbitrary concentration of an emulsion of two viscoelastic liquids has been performed in our laboratory by Palierne [5]. His expression reduces in the case of a dilute suspension to the generalization to complex modulus of a result given for Newtonian liquids by Oldroyd in a paper where he mentions the possible extension of his formula to complex viscosities [6]. The result for a volume fraction  $\phi$  of spherical inclusions  $I$  of radius  $R$  in the matrix  $M$  is

$$G^* = G_M^* \left( \frac{1 + 3\phi H}{1 - 2\phi H} \right) \tag{1}$$

$$H = \frac{4 \frac{\alpha}{R} (2G_M^* + 5G_I^*) + (G_I^* - G_M^*)(16G_M^* + 19G_I^*)}{\frac{\alpha}{R} (G_M^* + G_I^*) + (2G_I^* + 2G_M^*)(16G_M^* + 19G_I^*)}$$

Palierne's theory also provides extension to a distribution of size  $R$ , the term  $\phi H$  being replaced by  $\sum \phi_i H_i$ .

Close examination of Relation (1) reveals that although the elastic contribution due to the sphere deformation increases with  $\phi\alpha/R$ , the

relaxation time associated with this deformation increases with  $\alpha/R$ , so that this contribution is displaced toward higher frequencies and the quantitative analysis of the data to extract an accurate value of  $R/\alpha$  may become more difficult.

Graebling and Muller [7–9] carried out a systematic study of blends with different values of  $R/\alpha$  and shear moduli, and showed that the values fit reasonably the values of  $\alpha$  obtained from independent measurements (such as the falling drop or turning drop method [10, 11]) and the distribution of sizes obtained from SEM down to submicronic dimensions. A typical example [12] is given in Fig. 2 where the appearance of a new relaxation in the blend appears clearly in a Cole and Cole plot.

### NMR STUDY OF SMALL DIMENSION HETEROGENEITIES

The possibility of detecting and quantifying the presence of different phases by  $^1\text{H}$  NMR was first used in the study of semicrystalline polymers. It relies on differences in mobility of the two phases at temperatures between  $T_g$  of the amorphous phase and  $T_m$  (melting) of the crystalline phase. The former display a broad signal with full  $^1\text{H}$ – $^1\text{H}$  dipolar interaction, and the latter a narrow signal due to partial averaging of the dipolar interaction by the motion. Since the line shape is the Fourier transform of the time decay of the transverse magnetization, the free induction decay (FID) presents a fast decaying (crystalline) component and a slow decaying (amorphous) component which can be easily resolved [13, 14]. The same holds for any heterogeneous system where the two phases have different mobilities, in particular, in blends at temperatures between the  $T_g$ s of the two phases. Good agreement between the fraction of the rigid and mobile fractions and the known structure has been found in the case of block copolymers, a model system for blends, where not only the fraction but the dimensions of the cylindrical or lamellar structures are known from x-rays [15].

The determination of these sizes by NMR can be carried out by a large number of more or less elaborate techniques based on the relaxation of the longitudinal relaxation in the laboratory ( $T_1$ ) or rotary ( $T_{1\rho}$ ) frame and the concept of spin diffusion [16, 17].

The longitudinal relaxation time  $T_1$  measures the return of the initially disturbed spin system to thermal equilibrium. The rate of decay  $T_1^{-1}$  is essentially controlled by the Fourier component of the local magnetic

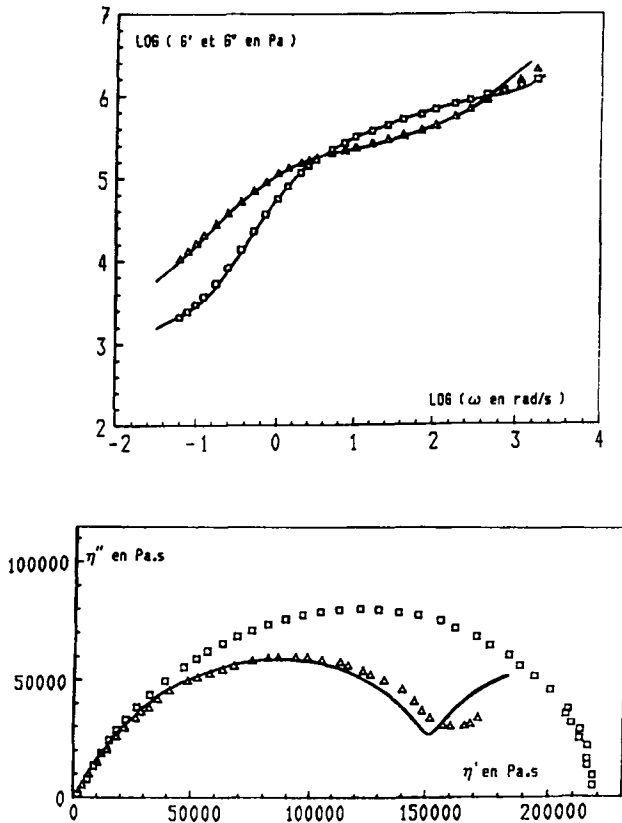


FIG. 2. Shear modulus of a blend with  $\phi = 0.25$  PS inclusions in a MMA matrix of higher viscosity ( $\eta_M/\eta_I = 46$ ) at  $180^\circ\text{C}$ . The lower curve shows the corresponding Cole and Cole plot (from Ref. 12). 2.5% of a block copolymer allows small sizes,  $R \approx 0.2 \mu\text{m}$ . The lines are calculated for  $\alpha = 1.3 \text{ mN/m}$ .

field fluctuation at the NMR Larmor frequency  $\gamma H_0$  of the observed nucleus. This rate is therefore generally higher in a mobile than in a rigid phase. In an heterogeneous blend with large inclusions, one expects a biexponential decay with the two  $T_1$  characteristic of the two pure components and relative amplitudes similar to what is observed in the decomposition of the FID.

When dealing, however, with small size inclusions, the decay of the longitudinal magnetization, or the decay of the spin-locked magnetiza-

tion in the rotatory frame (which is essentially controlled by the fluctuation of the local field at frequencies associated with the radio-frequency field,  $H_1$ , i.e.,  $\gamma H_1$ ) may become monoexponential or present a biexponential decay with very different amplitudes than deduced from the FID. This is due to the phenomenon of "spin diffusion" which allows for transport of magnetization from region of high magnetization to regions of low magnetization the same way as heat flows from a region of higher to a region of lower temperature. The spin diffusion constant  $D$ , which is again related to the strength of the  $^1\text{H}$ - $^1\text{H}$  dipolar interaction, can be evaluated from the line width [18]. If, therefore, one considers a model heterogeneous system with spherical inclusions of a rigid phase with a long  $T_1$  (or  $T_{1p}$ ) in a more mobile matrix with a short  $T_1$ , one can understand (Fig. 3) that after preparation putting the magnetization of the two phases in the same state of zero longitudinal magnetization (the same temperature), the longitudinal magnetization of the mobile phase recovers rapidly its equilibrium value while that of the rigid phase has not yet exchanged energy with the lattice. Magnetization then flows from the mobile to the rigid phase. One can assume very roughly that a layer of size  $(DT_1 \text{ rigid})^{1/2}$  recovers its spin magnetization by spin diffusion, so that only the rest of the material recovers with the typical  $T_1$  of the pure material. The amplitude of the slow component of the longitudinal magnetization relaxation will become smaller than the fast (rigid) component of the transverse magnetization relaxation (FID). If  $(DT_1)^{1/2}$  becomes of the order of the size of the inclusion, the longitudinal relaxation may become quasi-monoexponential. In that case, since  $T_1 > T_{1p}$ , the relaxation of the spin-locked magnetization in the rotatory frame may still remain biexponential.

A direct proof for the extent of spin diffusion can be obtained through the so-called Goldman-Shen sequence [19]. It uses the fact that during the FID, following a  $\pi/2$  pulse which transforms the longitudinal into transverse magnetization, the fast (rigid) component decays to zero while that of the slow (mobile) component still has a sizable value. It is then easy to transfer back the remaining transverse magnetization to the longitudinal axis, wait for a time  $\tau$ , and transfer again to the transverse direction in order to observe the new FID. If spin diffusion has taken place, this new FID again has a fast component, the amplitude of which measures the fraction of the rigid material corresponding to spin diffusion over a time  $\tau$ . Since a typical value of  $D$  in a rigid polymeric system is of the order of  $10^{-11} \text{ cm}^2/\text{s}$  and  $T_1$  values of the order of 1 s, one sees that NMR can detect the size of inhomogeneities when they are typically  $< 300 \text{ \AA}$ .

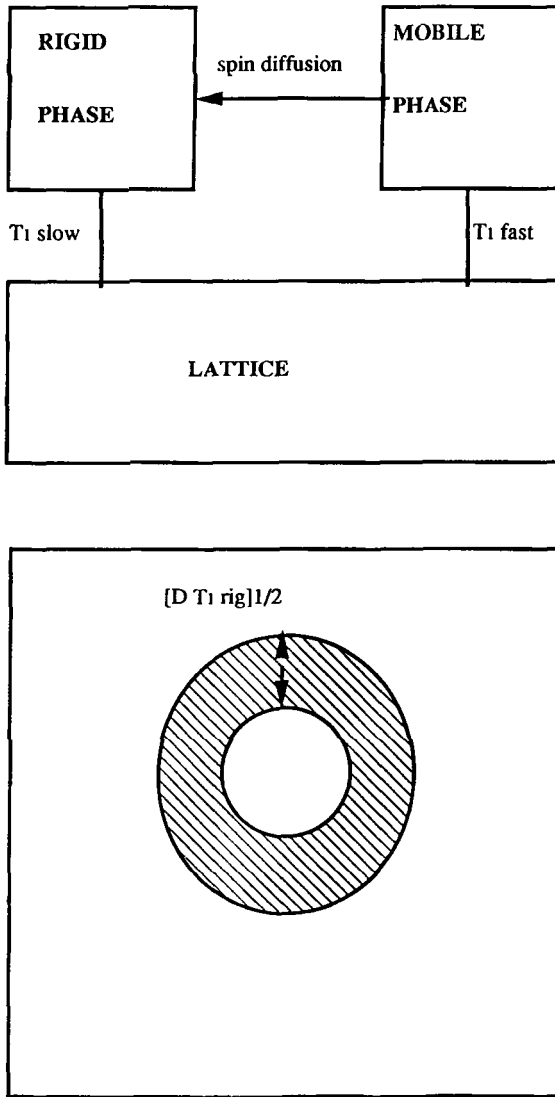


FIG. 3. Schematic representation of the magnetization recovery in the two phases through spin-lattice relaxation and spin diffusion. The magnetization of the mobile phase which recovers rapidly flows into the rigid phase at a distance of the order of  $(DT_{\text{rigid}})^{1/2}$ .



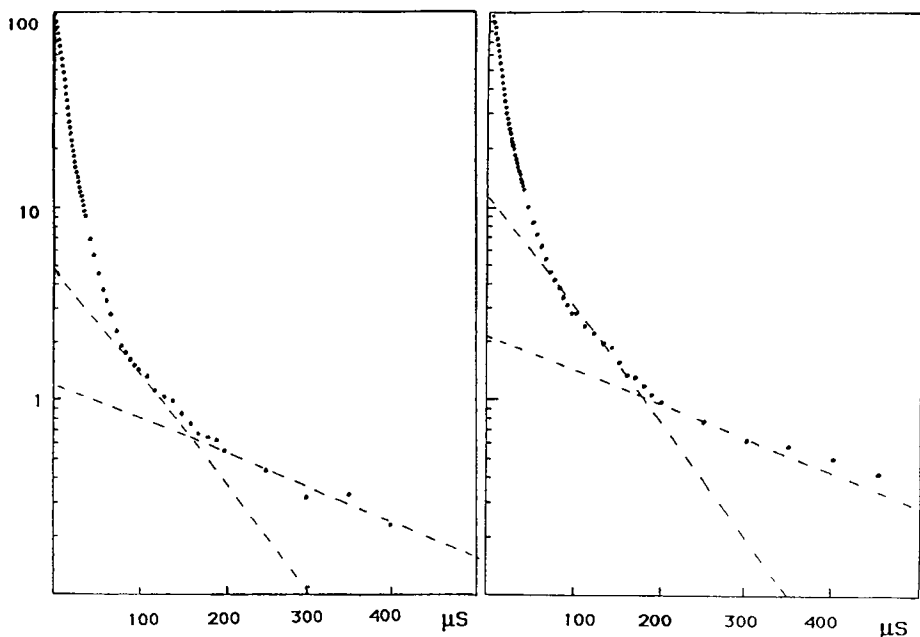


FIG. 4. FID from a 80/20 (left) and 60/40 (right) PMMA-PEO blend at room temperature (logarithmic scale).

Quantitative evaluations require assumptions on the geometry of the system to solve diffusion equations in 1, 2, or 3 dimensions.

With the advent of high resolution  $^{13}\text{C}$  NMR in solids [19], where the extent of  $^{13}\text{C}$  cross-polarization depends upon the magnetization of the protons in the immediate vicinity of the observed carbon, differences in proton spin dynamics in the two phases can be directly evaluated from the high resolution  $^{13}\text{C}$  signals belonging to one or the other of the two phases.

We illustrate the methods presented by the results carried out by Parizel on 40/60 and 20/80 blends of PEO and PMMA. These blends are compatible above the PEO melting point. Crystallization in the 40/60 blend is revealed by a DSC peak which is absent in the 20/80 blend. FID reveals, however, the presence of two phases in both blends (Fig. 4). The very small amount ( $\approx 1\%$ ) of a third component with a very long decay (narrow signal) can be attributed to residual water.

For the 40/60 blend, both the  $T_1$  and  $T_{1\rho}$  decays are biexponential

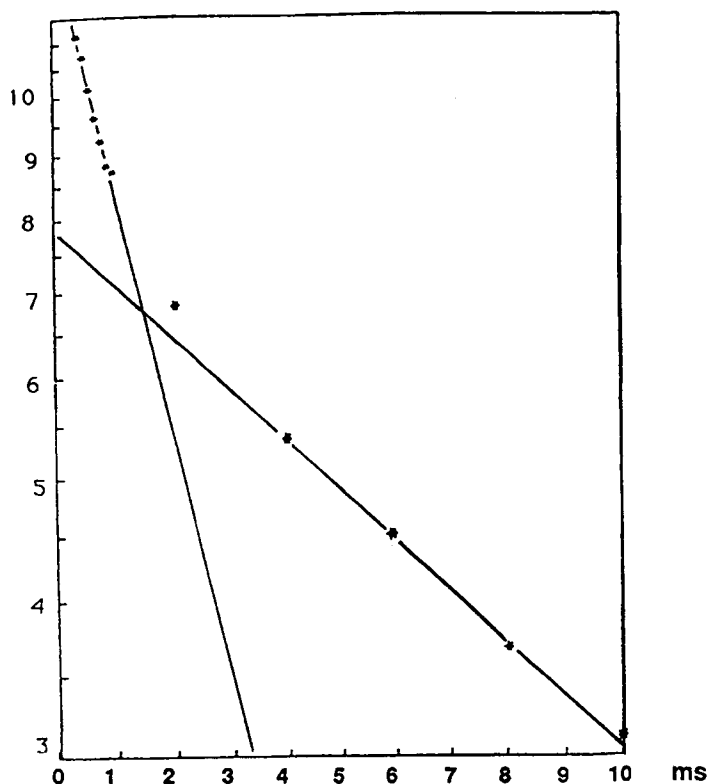


FIG. 5.  $T_{1\rho}({}^1\text{H})$  decay in the 60/40 PMMA-PEO blend.

(Fig. 5), with time constants and amplitudes close to that expected from the pure components, as a consequence of short  $T_1$  ( $\approx 0.1$ - $0.25$ ) and thick lamellae ( $L > 100$  Å) since, with  $D \approx 710^{-12}$  cm<sup>2</sup>/s,  $(DT_1)^{1/2} < 100$  Å.

For the 80/20 blends,  $T_1$  and  $T_{1\rho}$  decays are monoexponentials, revealing very small heterogeneities. Goldman-Shen experiments carried out both from direct  ${}^1\text{H}$  observation (Fig. 6) or from  ${}^{13}\text{C}$  observation (Fig. 7) reveal the effectiveness of spin diffusion and lead to an evaluation of the size of PEO heterogeneities in a 10 to 30 Å range of size.

More elaborate NMR techniques and methods of quantitative evaluation of the data are now being developed [21] which should extend the range of sizes which can be studied by NMR. The increased perfor-

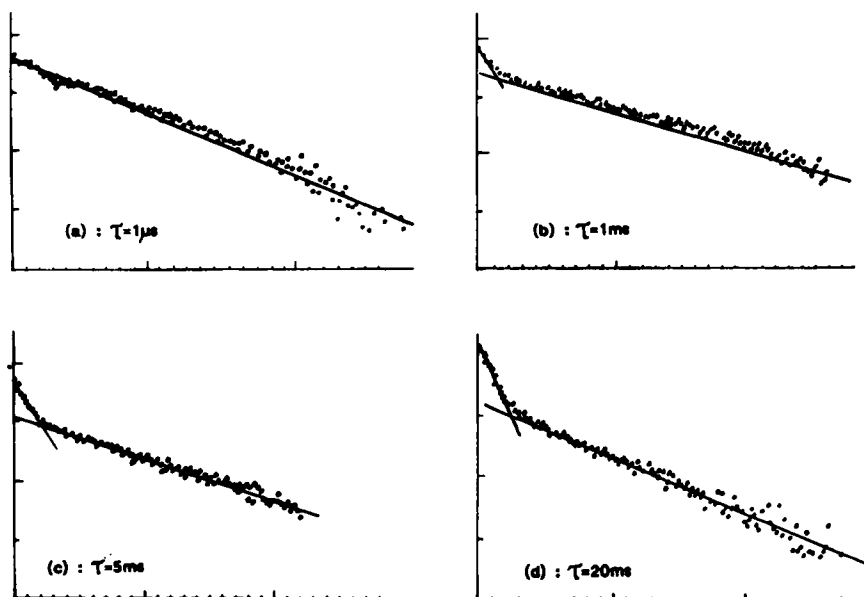


FIG. 6. Goldman-Shen method for a 80/20 PMMA-PEO blend. Recovery of the fast component of the  $^1\text{H}$  FID following spin diffusion during times from 1  $\mu\text{s}$  to 20 ms.  $T_1$  is monoexponential and equal to 230 ms.

Advances of standard instrumentation will certainly make them available to non-NMR specialists.

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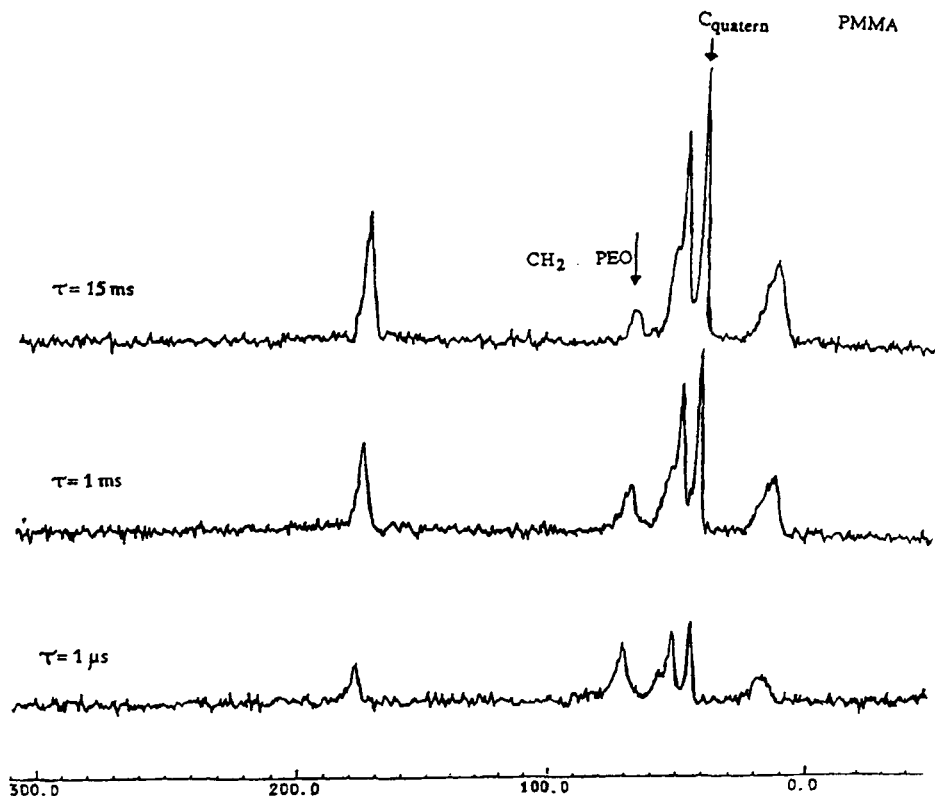


FIG. 7. Goldman-Shen method in high resolution  $^{13}\text{C}$ . The amplitude of the cross-polarized  $^{13}\text{C}$  signal reveals the magnetization of the attached  $^1\text{H}$ . The magnetization of the PMMA protons recovery is by spin diffusion from the PEO protons.

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